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Ordering of Interfacial Water Molecules at the Charged Air/Water Interface Observed by Vibrational Sum Frequency Generation

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Abstract

The molecular structure and orientation of interfacial water molecules at the air/water interface in the presence of soluble cationic and anionic surfactants has been characterized. We have employed vibrational sum frequency generation (VSFG) to probe the orientation of interfacial water molecules as a function of both bulk surfactant concentration and solution ion strength. The observed ordering of interfacial water molecules is manifested by an enhancement of the OH stretching modes in the VSFG spectra. We attribute the observed enhancement to an ordering of the interfacial water molecules induced by the large electrostatic field present at these charged interfaces. From the VSFG measurements we find that both the interfacial surfactant and water molecules attain their highest degree of order at sub-monolayer concentrations. The nature of this enhancement is further explored by studying mixed (cationic and anionic) surfactant systems as well as surfactant systems at different ionic strengths.

Introduction

Surfactants have found widespread uses in many industrial applications. Commercially available surfactants can be found in a range of products including motor oils, lubricants, detergents and soaps. In addition they are used in the manufacture of many common materials such as plastics and textiles and are also used in the oil industry for enhanced and tertiary oil recovery. From a biological standpoint, the structure and order of surfactants along with their interactions with other surface molecules play a crucial role in many processes. However, even with their widespread application, the molecular structure of surfactants as they reside at an oil/water,[1,2] air/water,[3-12] and solid/water[13-15] interfaces has only recently been determined. At present, there remains many unanswered questions concerning the physical behavior of surfactants at these interfaces. For example, at the water surface, where it is well known that the presence of a surfactant lowers the surface tension, experimental evidence for how the molecular structure of the highly coordinated surface water molecules changes with increasing surfactant concentration is nearly nonexistent. The focus of our work in this area is on providing insight into the molecular and ionic interactions which occur between surfactant and water molecules at an air/water interface.

In a previous letter[3] we described our recent results regarding the ordering and orientation of interfacial water molecules at the air/water interface due to the presence of cationic and anionic surfactants at the surface. Water molecules at the surface were found to be highly oriented, with the alignment resulting from the large electrostatic field created in the double layer region by the charged surfactant present at the water surface. These surface interactions were examined by employing the surface sensitive technique of vibrational sum frequency generation (VSFG) to measure the vibrational spectrum of *both* surfactant *and* water molecules at the air/water interface. The focus of the present paper is on further examination of these initial observations, in particular the effect of bulk

surfactant concentration and ionic strength on the order and orientation of interfacial water molecules. Complementing the water measurements will be spectroscopic studies of the relative order of the surfactant molecules at the air/water interface as a function of bulk concentration and ionic strength.

An aqueous solution of a soluble surfactant will have a certain number of surfactant molecules adsorbed at the water surface. The concentration of surfactant molecules at the surface, or the surface density, is dependent on the bulk surfactant concentration up to the point where a monolayer has formed on the surface. Once monolayer coverage has been reached the surface density generally remains constant with increasing bulk concentration below the critical micelle concentration. These surfactant molecules are amphiphilic and thus have a hydrophilic end, or head group, pointing into the water and hydrophobic end, or tail, pointing away from the water. For the surfactants studied here, the head groups of the surfactant molecules are charged which results in the formation of an electrostatic field in double layer region of the interface. Previous second harmonic generation (SHG) and VSFG studies at the charged quartz/water interface[16,17] have shown that water molecules near a charged interface are highly oriented. X-ray scattering studies at the charged electrode/water interface have also shown the interfacial water molecules to be highly oriented.[18,19] In pioneering second harmonic studies[20] of water/air interfaces, Eisenthal and coworkers attributed an observed change in the sign of the SH response from the water surface in the presence of insoluble cationic and anionic surfactants to the differing alignment of water molecules for the oppositely charged surfactants. However, since SHG lacks molecular selectivity under the nonresonant conditions of these earlier studies, little detail pertaining to the origin of the phase shift could be obtained. By being able to probe the vibrational structure of both the water molecules and the surfactant molecules at the air/water interface we have been able to show that water molecules are indeed highly oriented in the presence of charged surfactants and that the direction of orientation depends upon the surface charge of the surfactant.[3] We have attributed the ordering or alignment of

the interfacial water molecules to the electrostatic field in the double layer region produced by the surface charge. Since the direction of the electrostatic field is dependent on the sign of the surface charge we have studied the order of interfacial water molecules with both cationic and anionic surfactants present at the surface. Our studies provide direct evidence that the direction of the electrostatic field at the interface causes water molecules to align in opposite directions for the different surfactant charges. The opposing alignment is manifested by an interference between CH and OH stretching modes that is constructive for anionic surfactants and destructive for cationic surfactants. It is this interference between these vibrational modes as well as other spectral features which allow us to obtain unique insight into water-surfactant interactions at the air/water interface.

Background

Vibrational sum frequency generation (VSFG) is a nonlinear optical technique that has been extensively used in the study of surfaces and interfaces.[1,4,6,9] Since VSFG is a second order nonlinear process it is inherently surface sensitive. Further, for VSFG one combines a tunable infrared laser beam with a visible laser beam at a surface or interface. These two aspects of VSFG allow one to obtain a vibrational spectrum of molecules at an interface. The VSFG intensity is proportional to the square of the surface nonlinear susceptibility $\chi_s^{(2)}(\omega_{sfg}=\omega_{vis}+\omega_{ir})$ as

$$I_{sfg} \propto \left|P_{sfg}\right|^2 \propto \left|\chi_{NR}^{(2)} + \sum_v \left|\chi_{R_v}^{(2)}\right| e^{i\gamma_v}\right|^2 I_{vis}I_{ir} \qquad (1)$$

where P_{sfg} is the nonlinear polarization at ω_{sfg}, χ_{NR} and χ_{Rv} are the non-resonant and resonant parts of $\chi_s^{(2)}$, γ_v is the relative phase of the vth vibrational mode, and I_{vis} and I_{ir} are the visible and IR intensities. Since the susceptibility is in general complex the resonant terms in the summation are associated with a relative phase γ_v which is used to account for

any interference between two modes which overlap in energy. $\chi_{R_v}^{(2)}$ is also proportional to the number density of molecules, N, and the orientationally averaged molecular hyperpolarizability, β_v, as follows

$$\chi_{R_v}^{(2)} = \frac{N}{\varepsilon_0} \langle \beta_v \rangle. \tag{2}$$

Thus the square root of the measured SF intensity is proportional to the number density of molecules at the surface or interface. The molecular hyperpolarizability, β_v, is enhanced when the frequency of the IR field is resonant with a SF-active vibrational mode from a molecule at the surface or interface. This enhancement in β_v leads to an enhancement in the nonlinear susceptibility $\chi_{R_v}^{(2)}$ which can be expressed as

$$\chi_{R_v}^{(2)} \propto \frac{A_v}{\omega_v - \omega_{ir} - i\Gamma_v} \tag{3}$$

where A_v is the intensity of the vth mode and is proportional to the product of the Raman and the IR transition moments, ω_v is the resonant frequency, and Γ_v is the line width of the transition. Since the intensity term, A_v, is proportional to both the IR and Raman transition moments, only vibrational modes which are both IR and Raman active will be SF-active. Thus molecules or vibrational modes which possess an inversion center will not be SF-active. The fact that some vibrational modes are SF-active and some are SF-inactive has a direct consequence on the study of monolayers of surfactants with alkyl chains. Specifically, surfactant molecules which are in the all-trans conformation possess a local inversion center along the C-C bond which renders the CH_2 modes SF-inactive. However, this local inversion symmetry is removed when there are gauche defects along the alkyl chain and the CH_2 modes become SF-active. Comparison of the intensities of CH_2 and

CH_3 modes in the VSFG spectra has allowed researchers to monitor the relative order of various surfactants at the air/water[4,7-9], solid/water[13-15] and oil/water[1,2] interfaces.

In general the surface susceptibility $\chi_\sigma^{(2)}$ is a 27 element tensor, however it can often be reduced to several nonvanishing elements by invoking symmetry constraints. Liquid surfaces as well as monolayers on liquid surfaces are isotropic in the plane of the surface. The symmetry constraints for an in-plane isotropic surface reduces $\chi_\sigma^{(2)}$ down to the following four independent non-zero elements

$$\chi_{zzz}^{(2)}; \chi_{xxz}^{(2)} = \chi_{yyz}^{(2)}; \chi_{xzx}^{(2)} = \chi_{yzy}^{(2)}; \chi_{zxx}^{(2)} = \chi_{zyy}^{(2)} \tag{4}$$

where z is defined to be the direction normal to the surface. These four independent elements contribute to the VSFG under four different polarization conditions as follows

$$I_{ssp} \propto \left| F_i f_i f_z \chi_{iiz}^{(2)} \right|^2 \tag{5a}$$

$$I_{sps} \propto \left| F_i f_z f_i \chi_{izi}^{(2)} \right|^2 \tag{5b}$$

$$I_{pss} \propto \left| F_z f_i f_i \chi_{zii}^{(2)} \right|^2 \tag{5c}$$

$$I_{ppp} \propto \left| F_z f_i f_i \chi_{zii}^{(2)} + F_i f_z f_i \chi_{izi}^{(2)} + F_i f_i f_z \chi_{iiz}^{(2)} + F_z f_z f_z \chi_{zzz}^{(2)} \right|^2 \tag{5d}$$

where the polarizations are listed in the order of decreasing frequency (sf,vis,ir), the subscript i denotes x or y polarizations and F and f are the Fresnel coefficients for the reflected and incident waves respectively. The vibrational modes which are present under a certain polarization condition depends on the polarization of the IR field and the direction of the IR and Raman transition moments. The SSP polarization condition accesses vibrational modes with transition moments which have components in the plane perpendicular to the surface plane whereas the SPS and PSS polarization conditions accesses modes which have transition moments with components parallel to the surface plane. Since the intensity under PPP polarization conditions is dependent on all of the tensor elements, vibrational

modes with components both perpendicular and parallel to the surface plane will be present in the VSFG spectra. Most of the vibrational modes of interfacial molecules essential to the description of the systems studied here possess transition moments with components out of the plane of the surface. Consequently we primarily use the SSP polarization condition. However, verification of the peak assignments has been made from spectra using all of the polarization combinations.

At the charged air/water interface a significant surface charge exists which produces a large electrostatic field E_0. This electrostatic field can contribute to the non-linear polarization induced at the interface by the optical fields E_{vis} and E_{ir} through a third order polarization term $\chi^{(3)}$ as follows

$$P_{sfg} = \chi^{(2)} : E_{vis}E_{ir} + \chi^{(3)} : E_{vis}E_{ir}E_0. \tag{6}$$

Both $\chi^{(3)}$ and $\chi^{(2)}$ have resonant and non-resonant portions as described above and in fact the overall SF response can be described by an effective surface susceptibility which is a combination of $\chi^{(3)}$ and $\chi^{(2)}$. Second harmonic studies at the air/water interface with an insoluble charged surfactant present have shown that the third order polarization term is essential to the description of the overall polarization induced at the interface.[20] In addition these studies have shown that the SHG intensity is dependent on the magnitude of the electrostatic field which, in turn, is dependent on the surface charge density and the ionic strength of the surfactant solution. The electrostatic field can contribute to the SF response through the third order polarizability, $\alpha^{(3)}$, or through the removal of the centrosymmetry in the interfacial water molecular arrangement due to alignment of the water molecules. The reality of the interaction is certainly a combination of both effects.

In the experiments presented here we monitor the interfacial molecules, both surfactant and water, as the bulk surfactant concentration and solution ionic strength are varied. Changing the bulk surfactant concentration affects the surface concentration which

subsequently alters the surface charge density and thus the electrostatic field. Varying the ionic strength of the solution has a twofold effect on the electrostatic field for the soluble charged surfactants used in this study. One effect is a change in the Debye-Hückel screening length brought about by the change in the number of ions present at the interface. For example, as the ionic strength increases the number of ions at the interface increases and the surface charge is screened in a smaller distance. The smaller Debye-Hückel screening length means that fewer interfacial water molecules interact with the electrostatic electric field which in turn should produce a smaller third order nonlinear polarization. The other effect which is pertinent to the soluble surfactants used here is the surface concentration of the surfactant, and thus the surface charge density, which is dependent on the ionic strength of the solution. In general the surfactant surface concentration increases as the ionic strength increases up to a point and then remains constant with further increases in the ionic strength.

Experimental

The laser system employed for the vibrational SFG studies has been described in detail elsewhere.[21,22] Briefly it consists of a titanium:sapphire regenerative amplifier which pumps a two stage optical parametric amplifier seeded with a small portion of white light continuum. The system produces IR pulses tunable from 2.4 μm to 4.0 μm at a repetition rate of 1 kHz. The energy of the pulses over this range is approximately 10 μJ with a bandwidth of 18 cm^{-1} and a pulse duration of 1.9 ps. The IR pulses are combined at the interface with approximately 150 μJ of 800 nm light from the Ti:sapphire regenerative amplifier. All spectra presented were obtained under S_{sfg}, S_{vis}, P_{ir} polarization conditions with the 800 nm and IR beams directed onto the interface at an approximate angle of 56 and 68 degrees from the surface normal respectively. The generated sum frequency light is detected in reflection with a PMT after filtering. The spectra were collected with gated electronics and a computer. Each scan was obtained with an increment of 1 cm^{-1} and an

average of 200 laser shots per increment. The data was further averaged using the box averaging technique over a width of 9 cm^{-1}. This produced no change in the spectral information since the laser bandwidth was 18 cm^{-1}. In addition, for the spectra presented here only one out of every ten data points is plotted in an effort to make the figures easier to read.

Dodecylammonium chloride (DDA) was obtained from Eastman-Kodak and sodium dodecyl sulfate (SDS) was obtained from Sigma-Aldrich. Both surfactants were used as received without further purification and the solutions were made using HPLC grade water from Mallinckrodt. The surfactant solutions containing different ionic strengths were made by dissolving analytical reagent grade NaCl from Mallinckrodt in the HPLC water prior to dissolving the surfactant. A VSFG spectrum was obtained for each neat solvent at the air/solvent interface and the surface of the neat solvent at the air/solvent interface was determined to be relatively free of organic contaminant by an absence of peaks in the CH stretching region in the VSFG spectra. Surface tension studies were conducted to monitor the onset of monolayer formation as a function of bulk surfactant concentration. The surface tension measurements were obtained by the Wilhelmy balance method utilizing a platinum plate for SDS and a filter paper plate for DDA. The molecular area occupied by DDA and SDS at monolayer concentrations was found to be 35 Å^2 and 45 Å^2 respectively. Pentadecanoic acid (PDA) from Sigma was spread at the air/water interface by placing one drop of 1 mg/mL PDA in methanol on either a H$_2$O or D$_2$O surface with an area of 19.6 cm^2 which should place the monolayer in the liquid condensed (LC) phase. Further, at monolayer coverage in the LC region PDA has been shown to have a molecular area of approximately 25 Å^2 per molecule.[7] All experiments both surface tension and VSFG were conducted in a glass trough 55 mm in diameter.

Results and Discussion

A. Nonionic Surfactant

The relative order of alkyl surfactant molecules at an interface is typically gauged by the amount of gauche defects present in the alkyl chains. If the molecules at the interface are predominantly in the trans configuration they are assumed to have a high degree of order, whereas if many of the molecules have gauche defects the surfactant molecules are considered to have a lower degree of order. VSFG has previously been shown to be sensitive to the relative order of surfactant molecules at an interface.[1,2,7,8] As was mentioned earlier this sensitivity arises from the fact that for surfactant molecules in the all-trans configuration the CH_2 vibrational modes are SF-inactive. Thus the absence of CH_2 stretching modes in the VSFG spectrum from surfactant molecules at an interface is an indication of a high degree of order. Likewise, the presence of CH_2 stretching modes in the VSFG spectrum is indicative of gauche defects and correspondingly a lower degree of order. Another difference in the VSFG spectra from well ordered molecules and poorly ordered molecules appears in the CH_3 peak intensities under SSP polarization conditions. As was mentioned previously, under SSP polarization conditions the VSFG spectra will contain SF-active vibrational modes that have transition moments with components perpendicular to the plane of the surface. Surfactant molecules in the all-trans conformation which orient vertically to the liquid surface will have their CH_3 tails pointing out of the surface plane at an angle of 35 degrees from the surface normal and thus the CH_3 modes will have moments with components in the plane perpendicular to the surface plane. Surfactant molecules with gauche defects will have CH_3 tails lying in the plane of the surface and thus have CH_3 modes with moments that have smaller or no components perpendicular to the surface plane. Thus under the SSP polarization condition well ordered molecules will exhibit larger CH_3 intensities since they have a larger perpendicular component and molecules with a lower degree of order will have smaller CH_3 intensities due to a smaller perpendicular component. Through a comparison of the intensities of the CH_3 and CH_2 stretching modes from the VSFG spectra of alkyl surfactants at an interface

the relative order of the surfactants can be monitored. Table 1 shows the SF-active modes observed in VSFG studies under SSP polarization conditions along with the abbreviations used in this paper.

Pentadecanoic acid (PDA) on water has been studied previously by VSFG and has been shown to readily form a well ordered monolayer.[7,8] We use PDA here as an example of a well ordered monolayer and use its VSFG spectrum for comparison with spectra obtained from various other surfactants at the air/water interface. Figure 1 shows the SSP VSFG spectra from a monolayer of PDA on water under S-sfg, S-vis, P-ir polarization conditions. The PDA on water spectrum is dominated by two peaks which have been assigned to the CH_3 symmetric stretch, CH_3-SS (2875 cm^{-1}), and the CH_3 Fermi resonance, CH_3-FR (2935 cm^{-1}), of the symmetric stretch and overtones of the methyl bending modes.[7] There is little or no intensity from the CH_2 symmetric stretch, CH_2-SS, which has been observed to occur at 2850 cm^{-1}, or the CH_2 asymmetric stretch, CH_2-AS, which has been observed to occur at 2937 cm^{-1}.[1,14] As discussed above these characteristics are indicative of molecules with a high degree of order and few gauche defects.

Two other peaks appear in the PDA on water spectra which have not been observed in previous PDA studies. We assign these peaks to OH stretching modes from the interfacial water molecules. The first peak, designated OH-SS-S in Figure 1, is located at 3200 cm^{-1} and has been attributed to the coupled OH symmetric stretch from tetrahedrally coordinated water molecules at the interface.[17] This peak has been observed to have a strong intensity in the spectrum of ice and thus its strength is indicative of tetrahedral bond ordering in the molecular arrangement of water molecules or an "ice-like" structure.[17] Further, we have performed polarization experiments which indicate that the moment of the OH-SS-S mode is perpendicular to the surface plane. The other peak, designated OH-SS-A, is located at 3450 cm^{-1} and can be attributed to one of two possible modes: either the OH

symmetric stretch of asymmetrically hydrogen bonded water molecules[17] or water molecules with bifurcated hydrogen bonds.[23] The assignment of this mode is not crucial to the studies here since either assignment is indicative of bond disorder in the molecular arrangement or a "water-like" structure. Our polarization studies also indicate that the moment for the OH-SS-A mode is out of the plane of the surface. Previous studies have shown that by comparing the intensities of the OH-SS-S and OH-SS-A peaks one can infer the degree of OH bond ordering between the interfacial water molecules.[17]

B. Cationic Surfactant

Figure 2 shows the VSFG spectra at the air/water interface of dodecylammonium for several different bulk concentrations under S-sfg, S-vis, P-ir polarization conditions. Spectra were obtained from the air/water interface of solutions with bulk concentrations of 0.05 mM, 0.10 mM, 0.50 mM, 1.0 mM, 7.0 mM, and 14 mM DDA in water. Figure 2 shows the VSFG spectra from only the 0.05 mM, 1.0 mM, and 14 mM solutions. Figure 3 shows the square root of the VSFG intensity for the CH_3-SS, CH_3-FR, and OH-SS-S modes over the entire concentration range studied. We have performed surface tension measurements at the air/water interface of DDA solutions and find that the onset of monolayer formation occurs at a bulk concentration of approximately 5 mM, which agrees well with other data found in the literature.[24]

Upon inspection of the spectra in Figure 2 one notices the large enhancement of the OH stretching peaks in comparison to the spectrum of PDA on water. This enhancement increases for both peaks with increasing surfactant concentration. We attribute the enhancement to the large electrostatic field present at the interface due to the presence of the charged surfactant. Previous SHG studies of a charged surfactant at the air/water interface have shown an enhancement in the SH response[20] although these studies could not provide the type of molecular structure information shown here. Our results are also consistent with what has been observed previously in SHG and SFG studies at the charged

quartz/water interface[16,17] as well as X-ray scattering studies[19] at the charged electrode/water interface. The magnitude of the electrostatic field at monolayer concentrations, approximately 3 mM, can be as large as 10^7 V/m assuming a surface potential of 130 mV and a Debye length of 5.5 nm.[25]

The interaction between the electrostatic field, E_0, and the optical fields, E_ω, occurs through a third order coupling or a $\chi^{(3)}$ term in the expression for the nonlinear polarization induced at the interface. As was discussed earlier the $\chi^{(3)}$ term consists of a third order polarizability term, $\alpha^{(3)}$, and an orientational term, both of which are dependent on the magnitude of the electrostatic field. Since the SFG signal in the OH stretching region is dependent on the magnitude of electric field E_0, it is also dependent on the surface charge density or the surface concentration of the surfactant molecules. This dependence on the electrostatic field can be seen in the magnitude of the OH-SS-S peak which continues to increase as the bulk surfactant concentration increases reaching a maximum above 1 mM concentration. The behavior of the OH-SS-S intensity as a function of bulk surfactant concentration correlates well with increased surfactant concentration at the surface as determined from surface tension measurements. This correlation shows that the surface concentration of the surfactant impacts the relative ordering of water molecules manifested in an increase in the OH peaks in the VSFG spectra. Further, the OH-SS-S peak dominates over the OH-SS-A peak at all concentrations which implies an "ice-like" structure in the arrangement of the interfacial water molecules. Of particular interest in the OH enhancement is a destructive interference at approximately 2970 cm^{-1} which appears to be between the OH-SS-S mode and the CH_3-FR mode in the 2935 cm^{-1} region. We have used this interference, which is constructive for anionic surfactants, to infer the orientation of interfacial water molecules at positively and negatively charged interfaces.[3]

In studying the DDA surfactant structure, we find that the SF intensity in the CH stretching spectral region follows a trend similar to what is observed for the OH-SS-S peak from the water. As was mentioned earlier the number of molecules at the interface is proportional to the square root of the SF intensity and thus the SF intensity should correlate with the surface density as determined by surface tension measurements. Figure 3 shows the square root of the SF intensities of the CH_3-SS, CH_3-FR, and OH-SS-S peaks obtained from the VSFG spectra along with the surfactant surface coverage, the latter calculated from surface tension measurements plotted versus bulk surfactant concentration. Both the OH and CH_3 stretching modes show an increase in intensity with increasing surface concentration. The OH-SS-S peak grows as the bulk concentration increases because of the larger surface surfactant concentration and thus increased field at the interface. The CH_3 peaks grow with bulk surfactant concentration because the surface concentration increases and the surfactant molecules become more ordered with fewer gauche defects, both of which lead to an increasing VSFG signal. We find that for DDA molecules at the interface the highest degree of order observable is achieved before a complete monolayer has been formed as evidenced by the surface tension measurements and the CH_3 peak intensities. Coincidentally, from the OH-SS-S peak intensities the interfacial water molecules also appear to achieve the highest degree of order or alignment before monolayer formation. From the VSFG data we infer that both the interfacial water and the surfactant molecules have attained maximum order by a bulk concentration of approximately 1.0 mM and that the order does not change much beyond this point. The surface tension data however, shows that the surface surfactant concentration increases with increasing bulk surfactant concentration until a concentration of approximately 5 mM and then remains relatively constant. Another useful comparison in monitoring the relative order during monolayer formation is the ratio of CH_3-SS to CH_2-SS intensities as a function of bulk concentration. This comparison can be useful because as monolayer coverage is approached the carbon chains of the surfactant should become more ordered thus

decreasing the number of gauche defects. As the number of gauche defects is decreased the CH_2-SS intensity should also decrease which, in turn, causes an increase in the ratio of CH_3-SS to CH_2-SS intensities. Experiments at the oil/water interface have shown this ratio to be a good indicator of order as monolayer coverage is approached.[1,2] We are unable to use this ratio here due to the large bandwidth, 18 cm⁻¹, of the laser system employed which makes separating the CH_3-SS and CH_2-SS peaks impossible. We are in the process of decreasing the bandwidth of the laser system to approximately 5 cm⁻¹ so that comparisons of this nature can be made. However, even with the bandwidth limitations of the laser system we can observe the ordering of molecules during monolayer formation by monitoring the OH-SS-S, CH_3-SS, or CH_3-FR peaks.

C. Anionic Surfactant

Figure 4 shows the SSP VSFG spectra of SDS at the air/water interface at several different bulk surfactant concentrations. Spectra were obtained from solutions with bulk concentrations of 0.05 mM, 0.1 mM, 0.5 mM, 1.0 mM, 5.0 mM, 8.1 mM, and 10 mM. Figure 4 shows only the VSFG spectra from the 0.05 mM, 1.0 mM, and 8.1 mM SDS solutions. Figure 3 shows the square root of the VSFG intensity for the CH_3-SS, CH_3-FR, and OH-SS-S modes over the entire concentration range studied. We have performed surface tension measurements at the air/water interface of SDS solutions and found that monolayer formation occurs at approximately 2 mM. Our surface tension measurements and the concentration at which a monolayer forms agree well with literature values utilizing surface tension techniques[26] and radiotracer methods.[27]

The spectra in Figure 4 once again show the enhanced OH peaks that were present in the spectra of DDA on water. As was the case for DDA we attribute the enhancement in the OH peaks in the spectra of SDS on water to the static field present at the interface which aligns the interfacial water molecules. The size of the field at SDS monolayer concentrations is comparable to the field calculated for DDA (approximately 10^7 V/m).

However, for SDS, an anionic surfactant, the field points in the opposite direction and the difference in field direction is readily observable in the VSFG spectra in the region near 2970 cm^{-1}. Inspection of this region in the SDS spectra shows a constructive interference between the OH-SS-S and CH modes whereas in the DDA spectra the interference is destructive. In fact this constructive interference so enhances the CH$_3$-FR mode in the spectra from SDS on water that it dominates the spectra at all concentrations. We conclude that this change in the interference, constructive for anionic and destructive for cationic, is indicative of a flip in the water orientation at the interface produced by the difference in the field direction. For cationic surfactants one would expect the oxygen atom in the interfacial water molecules to be pointed towards the air and for anionic surfactants the oxygen atom to be pointed towards the bulk solution. As was the case with DDA, the OH-SS-S intensity from the SDS on water spectra reaches a maximum after about 1 mM bulk concentration. This is expected since the surface concentration and therefore the surface charge and electrostatic field reach a maximum after approximately 1 mM.

An important distinction between the ordering behavior of SDS and DDA can be found by further inspection of the SDS spectra versus bulk concentration data. Figure 5 shows the square root of the CH$_3$-SS, CH$_3$-FR, CH$_3$-AS, and OH-SS-S peak intensities along with the surface coverage as the bulk SDS concentration is varied. The surface coverage data was obtained from surface tension measurements. The CH$_3$-AS peak intensities were obtained from spectra with P-sfg, P-vis, P-ir polarizations not shown here. Inspection of Figure 5 shows that the OH-SS-S peak intensities correlate fairly well with the surface coverage data. From the OH-SS-S peak intensities and the surface tension data we find that the interfacial water molecules attain their highest degree of alignment before monolayer formation and the alignment is maintained at concentrations beyond a bulk concentration of 2.5 mM. The surface tension measurements show that the surface surfactant concentration increases with increasing bulk surfactant concentration up to a concentration of approximately 4 mM. In contrast to the behavior of the interfacial water

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molecules the intensity from the CH_3 peaks increases correspondingly with the surface tension measurements up to a bulk concentration of 2 to 3 mM. Beyond this point the SF data deviates from the surface tension data. In fact, each of the CH_3 peaks decreases in intensity beyond 1 mM with the CH_3-SS and CH_3-AS peaks having a comparable degree of decrease with increased concentration. The intensities from the CH_3-FR mode display a lesser degree of change with concentration. We attribute the slower rate of decrease of the CH_3-FR peak to the counteracting effect of the increasing OH-SS-S peak which constructively interferes or enhances the CH_3-FR intensity. The anomalous behavior of the CH_3 stretches might be explained by an increased disorder, e.g. an increased number of gauche defects, occurring above 1 mM or monolayer concentrations. The increased chain disorder could be caused by micelle formation which could interfere with the monolayer structure and contribute to a decrease in the CH_3 stretching intensities.

D. Mixed Surfactants

We have attributed the enhancement in the OH spectral region observed in the spectra from both DDA and SDS to the electrostatic field at the interface due to the charged surfactant. The magnitude of the enhancement should therefore be dependent on the strength of the field present which, in turn, should be dependent on the magnitude of the surface charge density. Consequently, one would expect that for an interface where the electrostatic field is zero, the enhancement would disappear. One way to test this prediction would be to examine an interface where there are approximately equal numbers of cationic and anionic surfactant molecules. Figure 6(a) shows the SSP VSFG spectra from the air/water interface of a solution of 0.02 mM DDA and 0.02 mM SDS. Clearly the OH peaks are not present in this spectra which is consistent with what we observe at the neat air/water interface. For comparison with the mixed surfactant case, Figures 6(b) and 6(c) show the SSP VSFG spectra from 0.05 mM SDS and DDA solutions respectively. In both the 0.05 mM SDS and DDA VSFG spectra the OH peaks are quite prominent. We attribute

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the disappearance of the OH peaks in the spectra from the mixed surfactant system to the cancellation of charge between the cationic and anionic surfactants and oppositely charged counter ions. The cancellation of surface charge leads to a much smaller field present at the interface and thus the interfacial water molecules are no longer aligned.

Along with the disappearance of the OH peaks in the VSFG spectra which occurs for the mixed surfactant system is an enhancement in the CH_3-SS and CH_3-FR peaks. This effect can be seen in a comparison of the CH_3-SS and CH_3-FR peaks from the mixed surfactant system, Figure 6(a), and the CH_3-SS and CH_3-FR peaks from the anionic, Figure 6(b), and cationic, Figure 6(c), surfactant systems. For both the anionic and cationic surfactants at bulk concentrations of 0.05 mM the CH_3 peaks are small and there is significant CH_2-SS intensity which suggests a low degree of order or a high number of gauche defects relative to higher bulk concentrations. The spectra from the mixed surfactant system however, is dominated by the CH_3-SS and CH_3-FR peaks indicating a higher degree of order or fewer gauche defects in the surfactant molecules. The greater interfacial order of the mixed surfactant system can be explained by ion pairing at the interface. The coulombic attraction of the oppositely charged surfactants allows them to pack closer and thus there is less volume for kinks in the tail groups.

E. Ionic Strength

Another factor that will affect the field present at the interface due to the surface charge is the ionic strength of the solution. Increasing the ionic strength of the solution decreases the Debye-Hückel screening length.[20,25] The decrease in the screening length is a result of the higher concentration of ions at the interface which screen the surface charge. The smaller Debye-Hückel screening length leads to fewer interfacial water molecules interacting with the static field which should have the effect of decreasing the third-order polarization. In changing the excess salt concentration from millimolar to molar concentrations the Debye-Hückel screening length can decrease by as much as 2 orders of magnitude or from approximately 40 nm at a ion concentration of 0.1 mM to 0.4 nm at an

ion concentration of 1.0 M. Assuming a nominal water diameter of 2 Å the number of layers of water molecules that interact with the field as the ionic strength is increased would go from approximately 200 at 0.1 mM to just 2 at 1.0 M. The effect of the ionic strength on the third-order polarization, $\chi^{(3)}$, has been observed in SHG studies of insoluble charged surfactants at the air/water interface.[20] The behavior of the SH intensity as a function of ionic strength has been attributed to the ordering of interfacial water molecules. However, since the SH intensity comes from both the interfacial water molecules and the surfactant molecules changes in the surfactant molecular ordering may also play a role. To provide a more detailed picture of the effect of ionic strength we have employed VSFG to study surfactant and water molecules independently at the air/water interface as a function of solution ionic strength.

Figure 7 shows the SSP VSFG spectra from 1.0 mM DDA solutions with varying ionic strengths. Spectra were obtained from 1.0 mM DDA solutions with 0.0 M, 0.05 M, 0.1 M, 0.5 M, and 1.0 M concentrations of excess NaCl. Inspection of the spectra shows that as the ionic strength is increased there is a clear reduction in the intensities of the OH stretching modes. This reduction illustrates the effect of increasing ionic strength on the orientation of interfacial water molecules which is a result of a decreased Debye-Hückel screening length. Specifically, as the ionic strength increases the Debye-Hückel screening length is shortened so that fewer water molecules can interact with the electrostatic field thus aligning fewer interfacial water molecules. Further, at NaCl concentrations above 0.5 M the OH peaks have diminished so much that the symmetric stretch from the NH_3^+ head group is visible around 3100 cm^{-1}. While the intensities of the OH stretches decrease with increasing ionic strength the intensities of the CH stretches remain relatively constant. The fact that the CH peaks remain relatively constant implies that the surface concentration of the DDA remains relatively constant. This observation has also been supported with surface tension measurements in this laboratory which show that the surface concentration

reaches a maximum above a NaCl concentration of approximately 0.2 M. Figure 8 is a graphical description of the behavior of the OH and CH peak intensities from the DDA spectra as a function of NaCl concentration.

Figure 9 shows the SSP VSFG spectra from 1.0 mM SDS solutions at varying ionic strengths. Spectra were obtained from 1.0 mM SDS solutions with 0.0 M, 0.05 M, 0.1 M, 0.5 M, and 1.0 M concentrations of excess NaCl. Once again the dependence of the Debye-Hückel screening length on the ionic strength is readily apparent in the OH peak intensities. As the ionic strength is increased the volume of water which interacts with the static field decreases and the SF intensity of the OH peaks decreases. The behavior of the CH peaks as the ionic strength is increased is not quite as straightforward due to the interference between these modes and the OH-SS-S mode. The CH_3-FR peak initially decreases with increasing ionic strength and then reaches a minimum above a NaCl concentration of 0.5 M thus implying a decrease in the surface concentration.

We have performed surface tension measurements on SDS as a function of ionic strength and have observed the surface concentration of SDS to increase with increasing ionic strength up to a concentration of approximately 0.1 M NaCl and then remains constant. The discrepancy between the surface tension data and the VSFG data can be explained by the interference between the CH_3-FR and the OH-SS-S peaks mentioned earlier. The interference is constructive for SDS, an anionic surfactant, and thus the CH_3-FR peak is enhanced by the presence of the OH-SS-S peak. This enhancement decreases when the OH-SS-S peak begins to diminish and continues up to NaCl concentration of 0.5 M which is the point at where most of the OH-SS-S intensity has disappeared. Thus the diminished enhancement, or the decrease in the CH_3-FR peak, results from the diminished OH-SS-S peak. The CH_3-SS peak initially goes down with increasing ionic strength and then goes back up after reaching a minimum at 0.1 M NaCl. The behavior of the CH_3-SS peak can also be explained in terms of the competing effects of increased surface concentration and diminished constructive interference from the OH-SS-S peak. For the

CH_3-SS peak the enhancement is smaller so that the negating of the enhancement by diminishing the OH-SS-S peak occurs at a lower NaCl concentration. Once the constructive interference between the CH_3-SS and OH-SS-S peaks no longer contributes to the CH_3-SS peak intensity the CH_3-SS peak intensity increases due to the increased surface concentration. Figure 10 is a graphical description of the peak intensities from the VSFG spectra of SDS as a function of NaCl concentration.

Conclusions

We have employed VSFG to show that the presence of charged surfactants at the air/water interface induces an alignment of the interfacial water molecules. The alignment of interfacial water molecules manifests itself in the VSFG spectra from the air/water interface by an enhancement in the OH stretching peaks which results from an electrostatic field produced by the charged surfactant molecules at the interface. By comparing the VSFG spectra from a cationic (DDA) and an anionic (SDS) surfactant we have been able to infer the relative orientation of the interfacial water molecules. Further, the difference in the interference between the OH-SS-S and the CH_3 modes for cationic and anionic surfactants is indicative of a flip in the orientation of the interfacial water molecules. X-ray scattering studies of the charged electrode/water interface have shown that the relative orientation of interfacial water molecules flips when going from a positively to negatively charged surface.[19] We postulate that for cationic surfactants at the air/water interface the oxygen atom of the interfacial water molecules is directed towards the air, whereas for anionic surfactants the oxygen atom of the interfacial water molecules is directed towards the solution. For the case of an aqueous solution where both cationic and anionic surfactants are present we find that the interfacial water molecules are not aligned in any particular direction and attribute this to a cancellation of surface charge and thus absence of the electrostatic field.

We have also shown that the degree of alignment of the interfacial water molecules is dependent upon the bulk concentration of charged surfactant as well the ionic strength of the aqueous surfactant solution. The alignment of the interfacial water molecules is dependent on bulk surfactant concentration because the surface surfactant concentration is dependent on the bulk surfactant concentration and the magnitude of the electrostatic field is dependent on the surface charge density. We find that for both DDA and SDS the interfacial water molecules are strongly aligned at bulk concentrations which are smaller than the bulk concentrations at which surface tension measurements indicate a monolayer to have formed. The effect of the ionic strength of the solution on the electrostatic field and thus the alignment of the interfacial water molecules can be understood in terms of a screening of the surface charge or a change in the Debye-Hückel screening length. We find that the alignment of the interfacial water molecules decreases as the ionic strength of the solution increases as evidenced by a decrease in the enhancement of the OH stretching peaks in the VSFG spectra. The decrease in the alignment of the interfacial water molecules with increasing ionic strength is attributed to a shortening of the Debye-Hückel screening length which limits the number of interfacial water molecules that can interact with the electrostatic field. For the extreme case of little or no electrostatic field present at the interface one expects the interfacial water molecules not to be oriented and we have observed this lack of orientation as evidenced by the absence of OH stretching modes in the VSFG spectra from the mixed cationic and anionic surfactant system.

The relative order of the surfactant molecules at the air/water interface has also been accessed by employing VSFG to monitor the CH stretching region of the surfactant molecules. We find that the nonionic surfactant pentadecanoic acid forms the most ordered monolayer of the surfactants studied followed by the mixed surfactant, the dodecylammonium, and the dodecyl sulfate monolayers listed in order of decreasing surfactant chain order. In addition, by monitoring the CH stretches in the VSFG spectra we can follow the onset of monolayer formation for DDA at the air/water interface but find

this process to be complicated for following the onset of monolayer formation of SDS due to the constructive interference between OH and CH stretches in the VSFG spectra from SDS. A more detailed analysis of the surfactant structure including accessing more molecular modes in the surfactant molecules is forthcoming with planned modifications of the laser system for bandwidth reduction and extended infrared tunability.

Table and Figure Captions

Table 1

Frequencies and designations for SF-active modes observed under SSP polarization conditions in VSFG spectra from various interfaces.

Figure 1

VSFG spectra under SSP polarization conditions of the air/water interface of a monolayer of pentadecanoic acid (PDA) on water. Solid lines are a guide to the eye.

Figure 2

VSFG spectra under SSP polarization conditions of the air/water interface of solutions of various bulk concentrations of DDA in water. Bulk concentrations of 0.05 mM, 1.0 mM, and 14 mM only are shown. Solid lines are a guide to the eye.

Figure 3

CH_3-SS, CH_3-FR, and OH-SS-S peak intensities from Figures 2(a) and 2(b) with the surface coverage from surface tension measurements for DDA at different bulk surfactant concentrations. Solid lines are a guide to the eye.

Figure 4

VSFG spectra under SSP polarization conditions of the air/water interface of solutions of various bulk concentrations of SDS in water. Bulk concentrations of 0.05 mM, 1.0 mM, and 8.1 mM only are shown. Solid lines are a guide to the eye.

Figure 5

CH$_3$-SS, CH$_3$-FR, CH$_3$-AS and OH-SS-S peak intensities from Figures 4(a) and 4(b) with the surface coverage from surface tension measurements for SDS at different bulk surfactant concentrations. Solid lines are a guide to the eye.

Figure 6

(a) VSFG spectra under SSP polarization conditions of the air/water interface of an aqueous solution of (a) 0.02 mM DDA and 0.02 mM SDS, (b) 0.05 mM DDA, and (c) 0.05 mM SDS. Solid lines are a guide to the eye.

Figure 7

VSFG spectra under SSP polarization conditions of the air/water interface of a 1.0 mM solution of DDA with 0.0 M, 0.05 M, 0.1 M, 0.5 M, and 1.0 M excess NaCl. Solid lines are a guide to the eye.

Figure 8

CH$_3$-SS, CH$_3$-FR, and OH-SS-S peak intensities from Figure 7 as a function of ionic strength. Solid lines are a guide to the eye.


Figure 9

VSFG spectra under SSP polarization conditions of the air/water interface of a 1.0 mM solution of SDS with 0.0 M, 0.05 M, 0.1 M, 0.5 M, and 1.0 M excess NaCl. Solid lines are a guide to the eye.

Figure 10

CH$_3$-SS, CH$_3$-FR, and OH-SS-S peak intensities from Figure 9 as a function of ionic strength. Solid lines are a guide to the eye.

| Designation	Mode	Frequency (cm^{-1})	Reference
CH$_2$ SS	Symmetric Stretch	2850	(2)
CH$_3$ SS	Symmetric Stretch	2875	(7)
CH$_2$ FR	Fermi Resonance	2917	(2)
CH$_3$ FR	Fermi Resonance	2935	(7)
N$^+$-H Str.	N$^+$-H Symmetric Stretch	3100	This Study
OH SS-S	Sym. Stretch Sym. Coord. H$_2$O	3200	(17)
OH SS-A	Sym. Stretch Asym. Coord. H$_2$O	3450	(17)
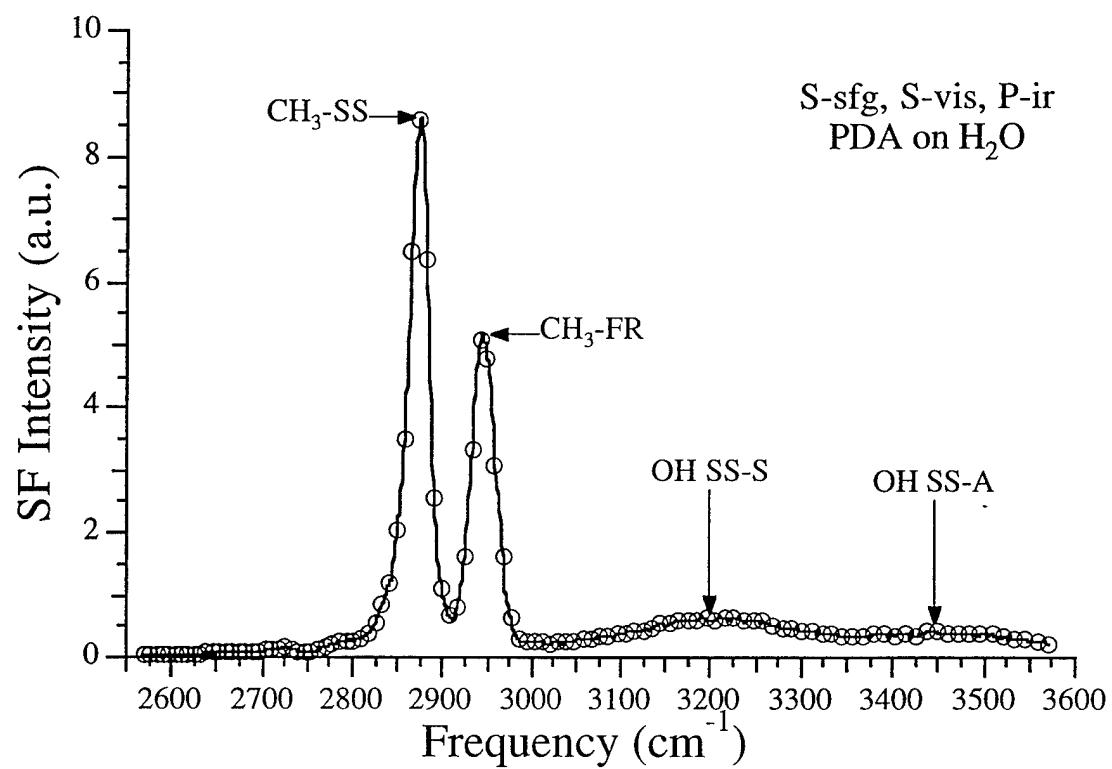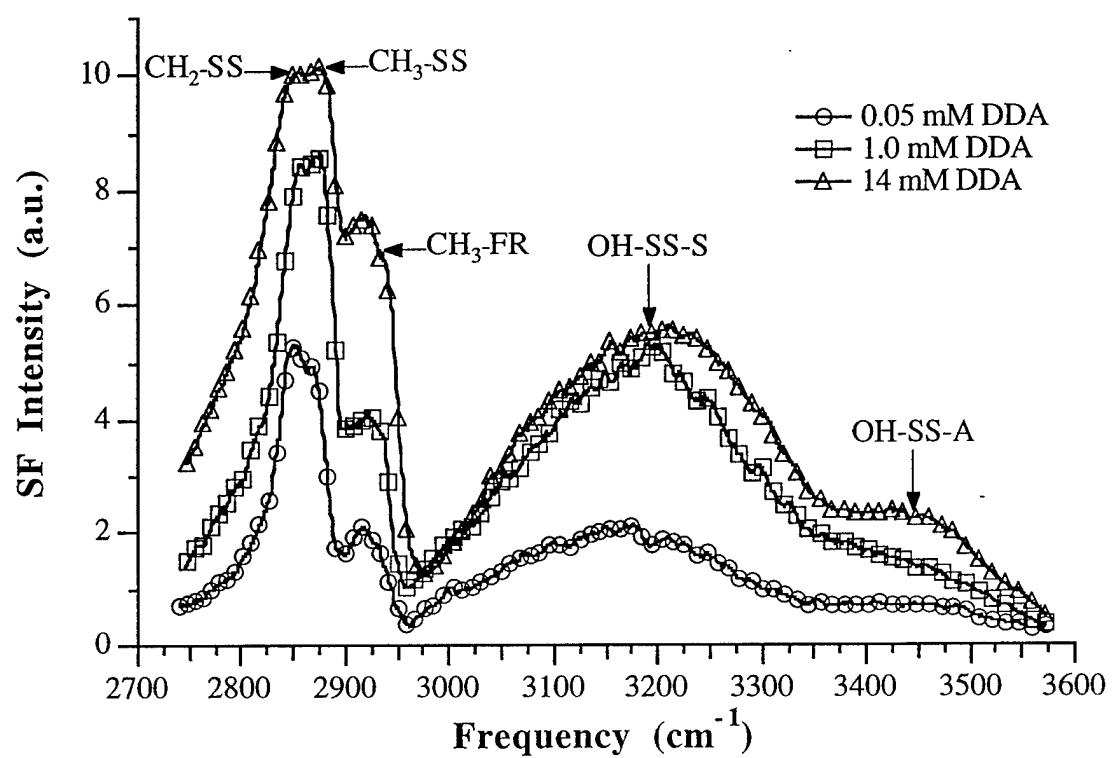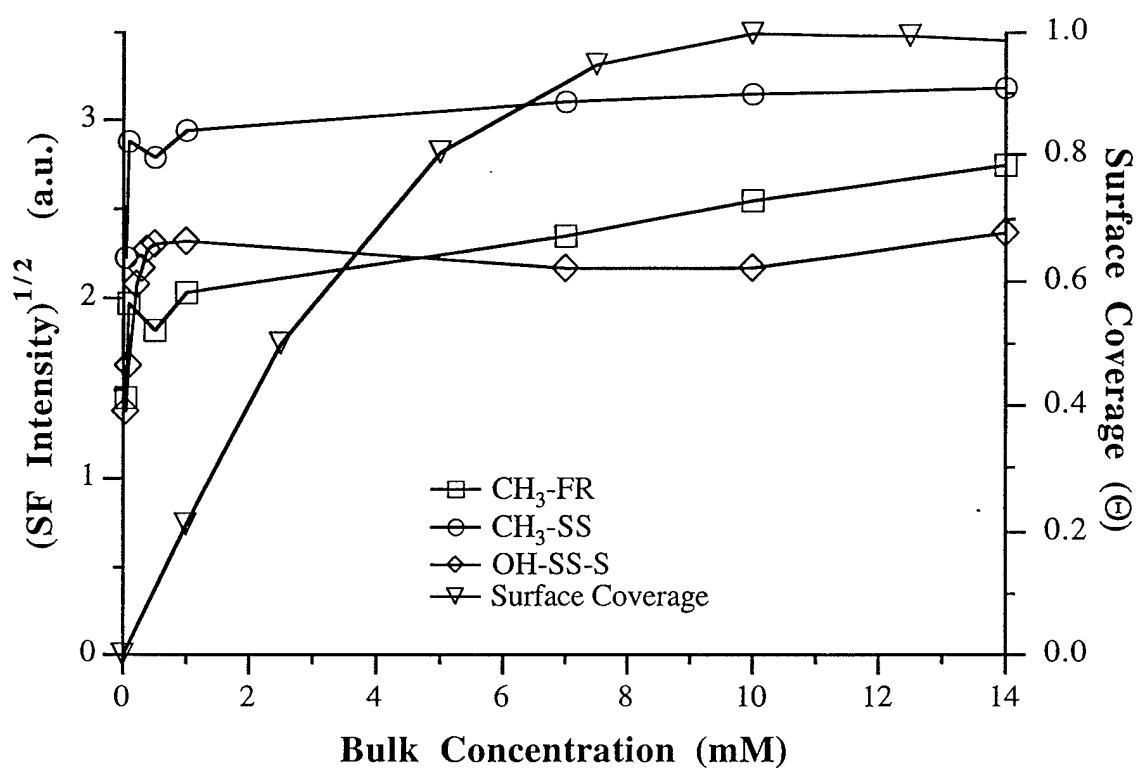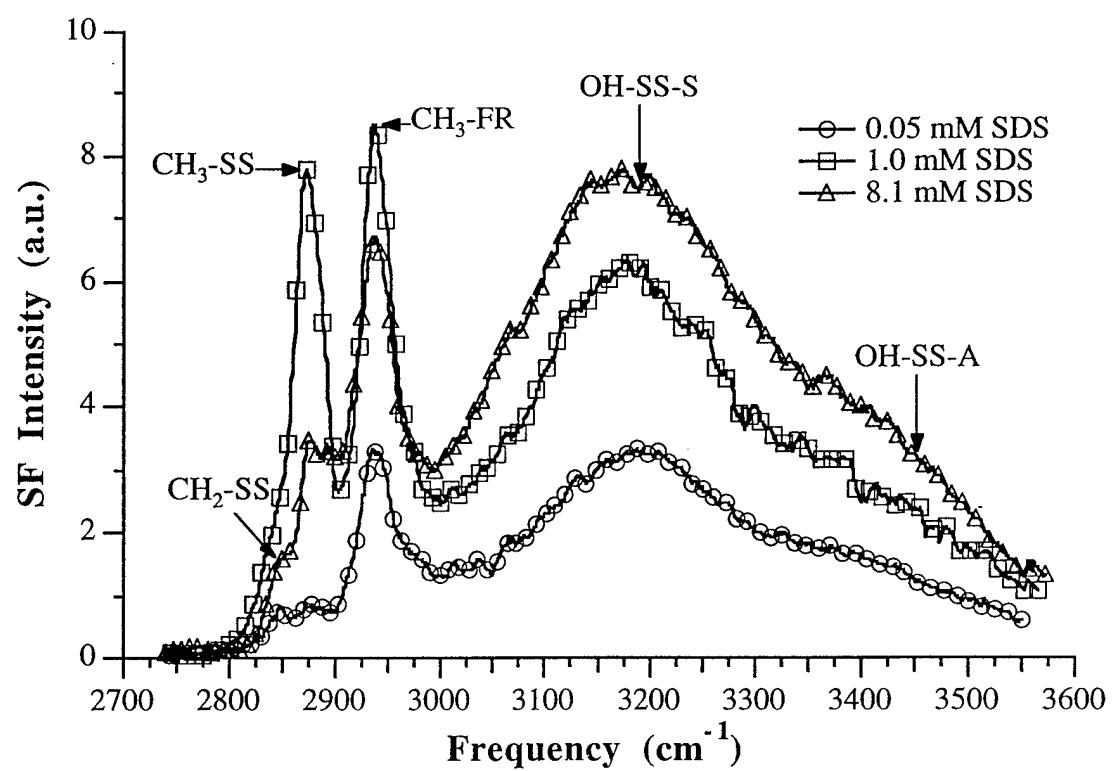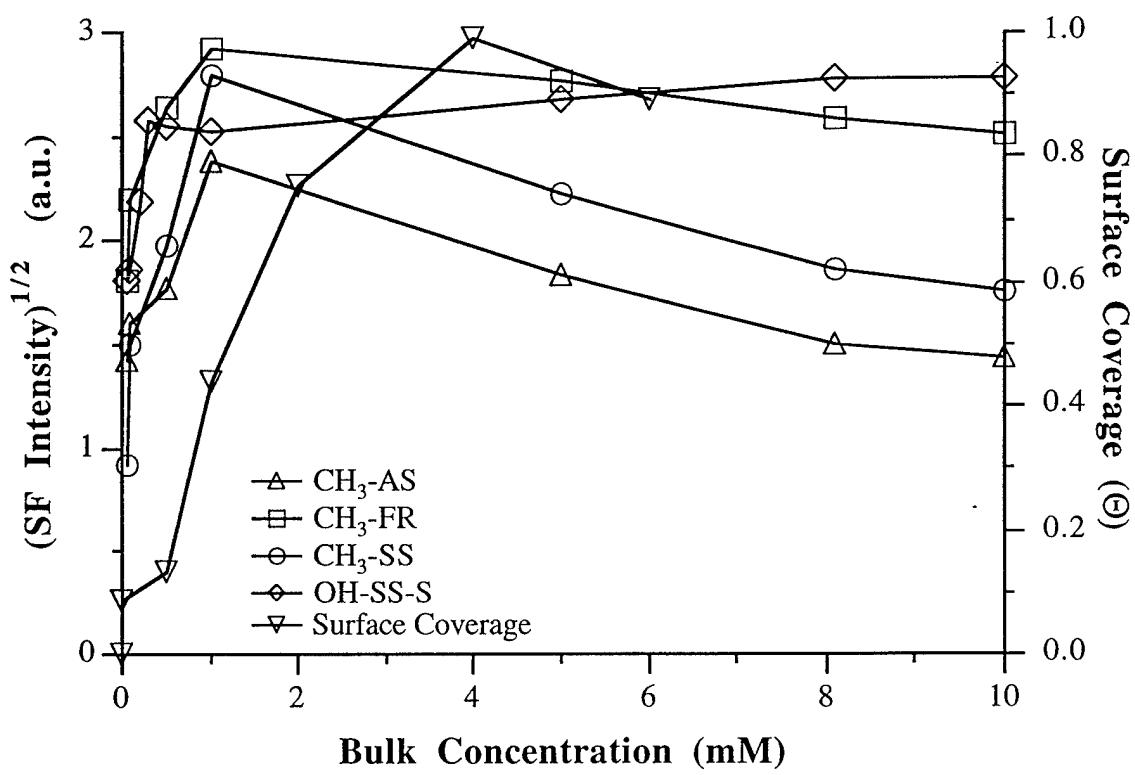
Figure 6
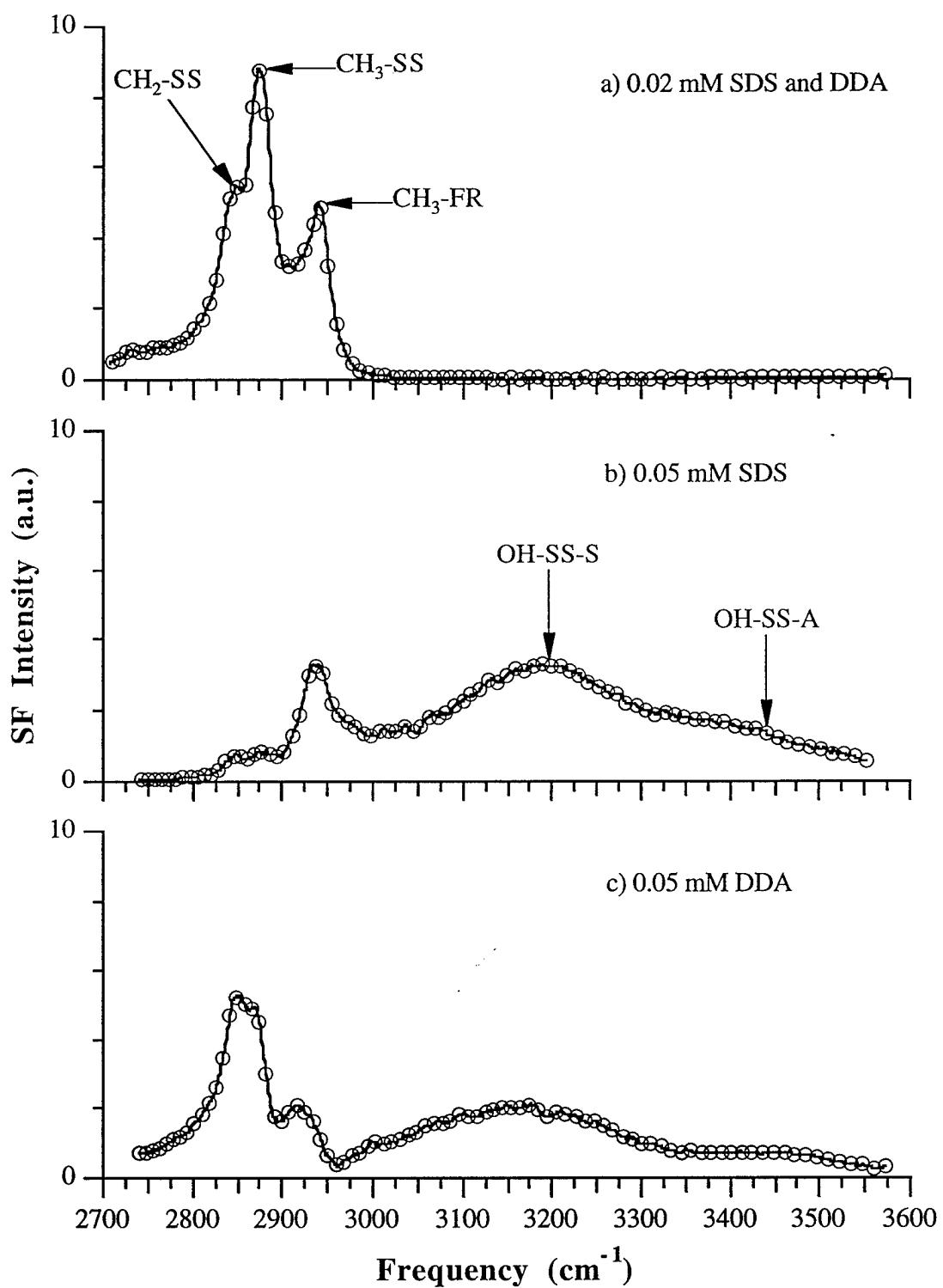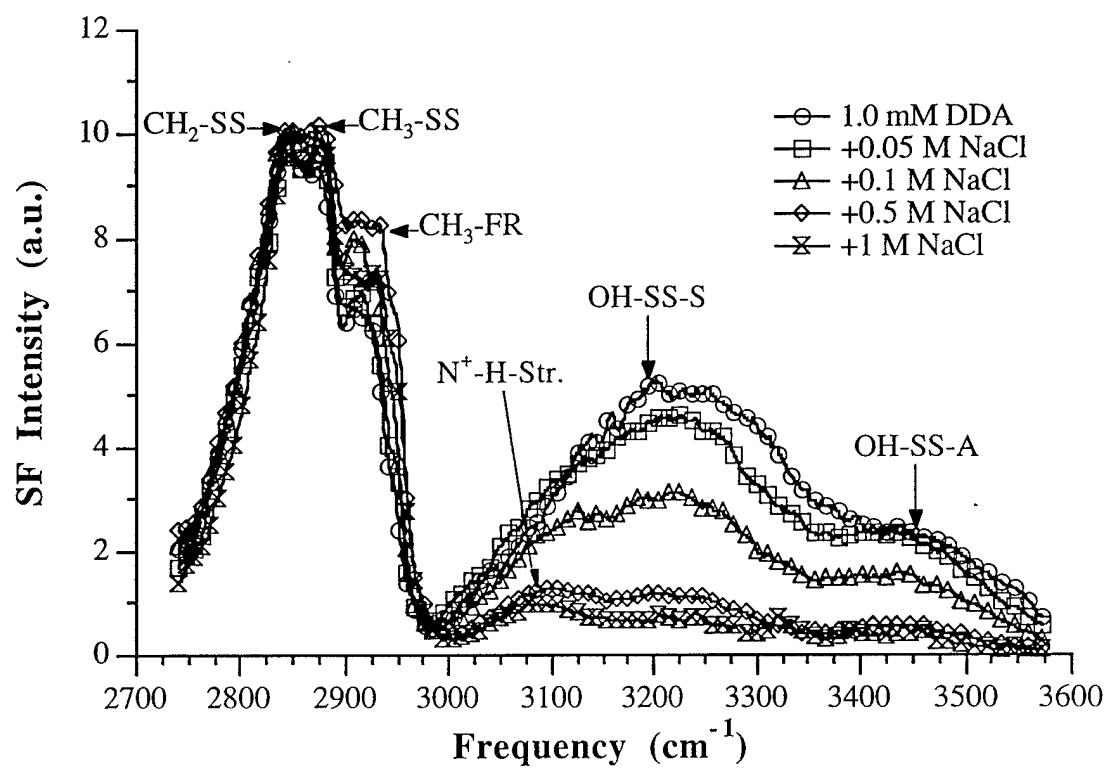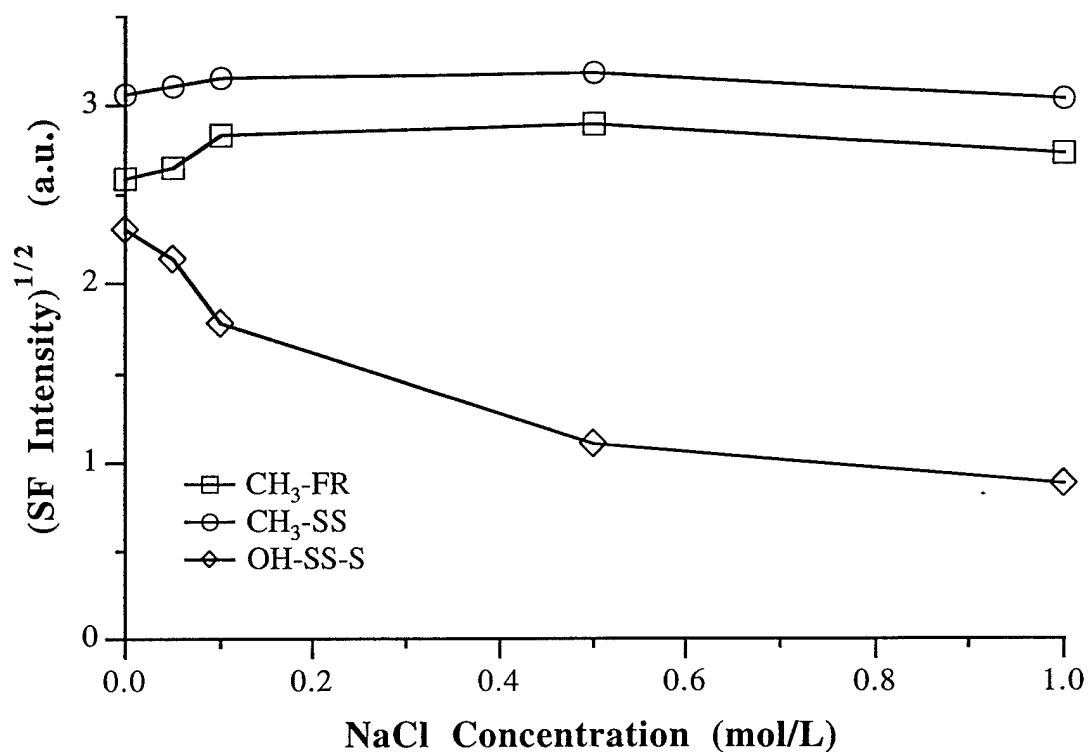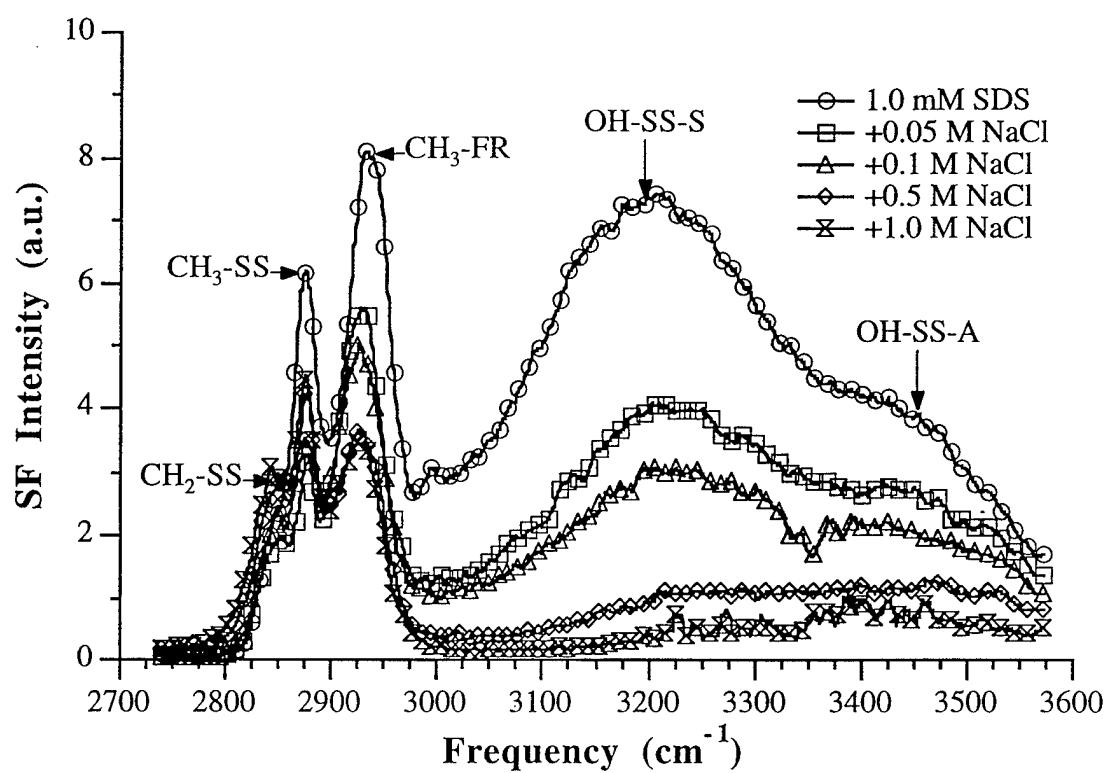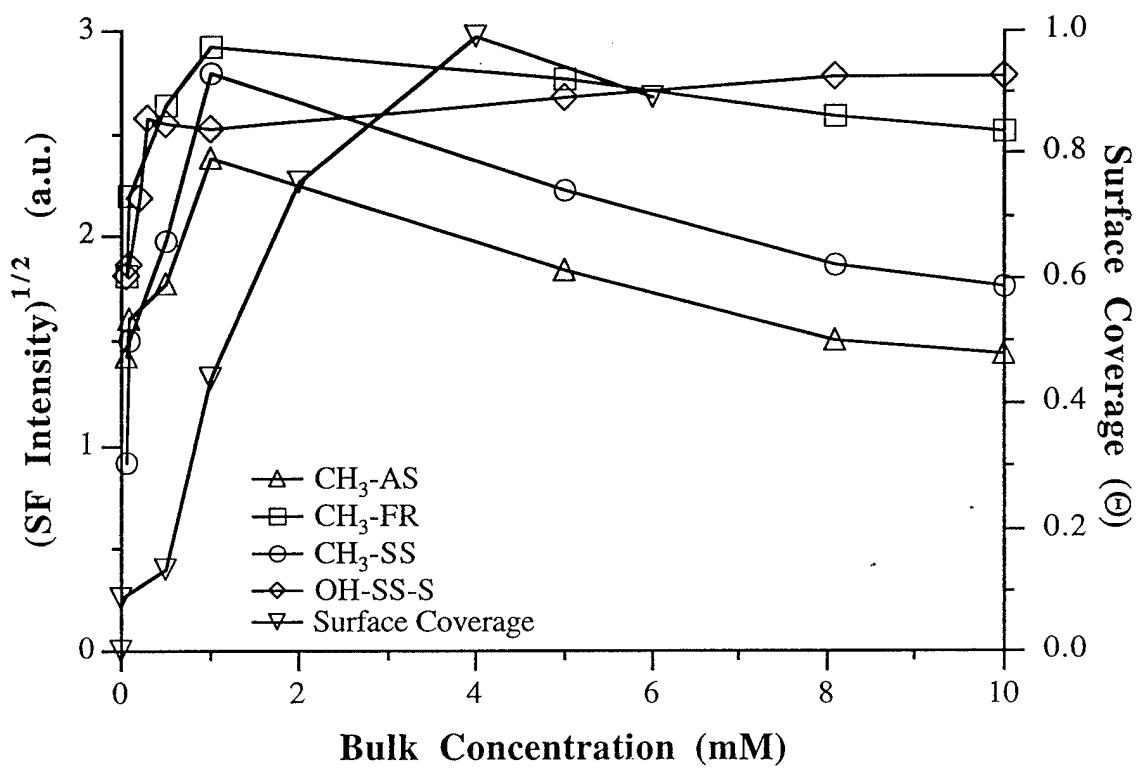
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